Indian J. Phys. **54B**, 484–489 (1980)

Molecular force field for sulphur tetrafluoride

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Received 1 November 1978

Abstract: The potential energy constants of SF_4 molecule have been calculated using a modified kinematic procedure. The matrix B, that diagonalises G, the inverse kinetic energy matrix is so chosen using a matrix operator T, as to lead to a reasonably good set of potential field of the molecule. The mean amplitudes of vibration calculated using these force constants compare well with the electron diffraction data.

1. Introduction

In the normal coordinate analysis of polyatomic molecules, kinematic methods (Torkington 1949, Herranz and Castano 1966, Billes 1966, Strey 1967, Freemann 1968, Sawodny 1969, Pfeiffer 1969) have been found to be very useful in approximately fixing the force field of a molecule One of the kinematic methods suggested by Herranz and Castano (1966) gives more reasonable set of potential energy constants in a number of molecules studied by one of the authors (Ramaswamy and Rao 1969a, 1969b, 1969c). In this method the matrix of transformation L^{-1} from the symmetry to the normal coordinates is obtained from the relation

$$L^{-1} = BM^{\frac{1}{2}}B' \tag{1}$$

where $M^{\frac{1}{2}}$ is a diagonal matrix with its elements as the reciprocals of the square root of the positive eigen-values of G, B is an orthogonal matrix that further satisfies

$$B'GB = M^{-1}. \tag{2}$$

The prime over B denotes its transpose. In the above equation M^{-1} is a diagonal matrix whose elements are the eigenvalues of G the inverse kinetic energy matrix in proper order along the diagonal. But one usually initially obtains a matrix B_0 that satisfies the relation

$$B'_0GB = M_0^{-1} \tag{3}$$

where M_0^{-1} is a diagonal matrix, whose diagonal elements are the eigenvalues of G, in random order along the diagonal. In order to obtain the matrix B that diagonalises G, to reproduce its eigenvalues satisfying equation 2 above, we may write

$$B = B_0 T \tag{4}$$

where T is a matrix operator which merely orders the columns of B_0 matrix so as to satisfy the equation (2). This modified procedure has been found to give a unique set of potential energy constants in the case of groupV hydrides (Rao and Vellaswamy 1979). An attempt is made to extend this modified procedure to the SF_4 molecule with a view to get a set of potential energy constants and check the validity of this modified procedure

According to the electron pair repulsion theory (Gillespie 1962), SF_4 has a trigonal bipyramidal structure with a lone pair of electron occupying an equatorial site. The band angles and distances reported by Tolles and Gwinn (1962) have been used in the present calculations. The vibrational frequencies assigned to the molecule on the basis of C_{2v} symmetry by Dodd *et al* (1956) have been used to obtain the potential energy matrix elements. These are given in Table 1.

Table 1. Molecular parameters and vibrational wave numbers for SF_4

Molecular parameters		Species	Vibrational Wave numbers (cm^{-1})
a (axial distance)	1·646 A	a_1	715, 889, 557, 235
d (equatorial distance)	1·545 A	a_2	401
β F'SF	86° 32′	b_1	867, 532
η FSF	101° 33′	b_2	728, 463

F-equatorial atom, F'—axial atom.

2. Potential energy constants

The symmetry coordinates and G, the inverse kinetic energy matrix elements used here are essentially the same as that given by Krishna-Pillai *et al* (1965). The residual G matrix obtained after removing the elements having infinite values in the G matrix owing to the presence of zero mass lone pair, is used to

determine the potential energy matrix, by the modified procedure outlined earlier. In the case of SF_4 molecule, the T matrix satisfying the relation 2 given earlier for the different symmetry species are as follows.

For a_1 species

$$T = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

For b_2 species

$$T = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

For b_1 species

$$T = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \tag{5}$$

Now after evaluating the B matrix, the L^{-1} matrix can be obtained. The potential energy matrix was then obtained using the relation

$$F = L^{-1'} \Lambda L^{-1} \tag{6}$$

where Λ is a diagonal matrix with elements given by

$$\lambda_k = 4\pi^2 C^2 \nu_k^2 \tag{7}$$

in which ν_k is the frequency of the K-th normal mode in cm^{-1} and C is the velocity of light.

The symmetrical F elements and the valence force constants obtained by this method are presented in Table 2.

3. Mean amplitudes of vibration

The mean square amplitude matrix Σ was obtained using the relation (Cyvin 1959)

$$\Sigma = L\Delta L' \tag{8}$$

where Δ is a diagonal matrix with elements given by

$$\Delta_k = \frac{}{8\pi^2 C\nu_k} \coth \frac{hC\nu_k}{2KT} \tag{9}$$

Table 2. Potential energy constants for SF_4. (The F matrix elements containing only stretching constants are in mdyn/A, those containing only angle-angle constants are in mdyn A/rad^2 and those containing bond angle interactions are in mdyn/rad.)

Symmetry Species	F Elements Present Work	(Krishna Pollai *et al* 1965)	Valence force constants in mydn/A Present Work		Modified UBFF Constants in internal coordinates (Krishna Pillai *et al* 1905)
	F_{11}	5·73858	6 4072		
	F_{22}	7·23133	5·3768		
	F_{33}	4·09887	0·7364		
	F_{44}	1·98367	6·2097	f_a	4·58110*	4·7237
	F_{12}	−0 29079	1·2645	f_d	6·44180	5·1347
a_1	F_{13}	0·14803	0·0000	f_{dd}	0·78952	0·2421
	F_{14}	0·04645	0 9306	f_{ad}	−0·14539	0·6324
	F_{23}	0·96477	0·2213	f_γ	4·09887	0·7364
	F_{24}	1 63387	·8334	f_β	2 51482	3·4467
	F_{34}	−1·55500	0·0000	$f_{d\beta}$	0·02788	·5893
	F_{88}	5·65228	4·8926	$f_{\alpha\beta}$	0·46157	0·5789
b_2	F_{99}	3·24828	4·6097			
	F_{89}	−1·80835	0·8334			
a_2	$F_{11,11}$	1·40370	1·4037			
	$F_{12,12}$	3·42363	3·0401			
b_1	$F_{13,13}$	1·70090	1·5635			
	$F_{12,13}$	1·25906	0·7068			

This number of significant figures is retained to secure internal consistency in the calculations.

in which h is the Planck's constant, K is the Boltzmann's constant and T is the absolute temperature in °K. The symmetrized Σ matrix contains the mean amplitude quantities σ of the bond and non-bond distances The important mean square amplitudes were evaluated using the relations given by Krishna Pillai *et al* (1965) The results are given in Table 3.

Table 3. Mean Amplitude of Vibration of SF_4 at 298.16K

Mean Square Amplitude Matrix elements $(Å)^2$	Mean Square Amplitude $(Å)^2$	Mean Amplitude (Å)	Electron Diffraction Data. (Dodd *et al* 1956)
Σ 11 0·001251			
Σ 22 0·001698	σ_a 0·002003	0·04475	0·04440 0·047±0·005
Σ 33 0·002956	σ_d 0·001744	0·04176	0·04015 0·041±0·005
Σ 44 0·001813	σ_η 0·002956	0·05437	0·09276
Σ 55 0·001791	σ_β 0·002596	0·05095	0·04875
Σ 66 0·002002	$\sigma_{FF'}$ 0·004663	0·06828	0·06991 0·067±0·005
Σ 77 0·002837	σ_{FF} 0·007292	0·08539	0·09954 0·068±0·010
Σ 88 0·002755	F-equatorial atom.		
Σ 99 0·003733	F'-axiyl atom.		

4. Discussion

It is seen from Table 2 that the value of the axial stretching force constant is less than the equatorial stretching force constant and this is consistent with the bond length force constant relation The value of F_{33} is higher than F_{44} in the present calculation and this may be expected since F_{33} represents only the bending between the two equatorial fluorine atoms influenced by the presence of lone pair of electron in the equatorial site. A similar trend is also noticed in the equatorial and axial bending force constants $\bar{f}_\eta$ and $\bar{f}_\beta$ respectively It may be interesting to observe that just as the equatorial stretching force constant is higher than the axial stretching force constant, the equatorial bending force constant $\bar{f}_\eta$ is also greater than the axial bending force constant $\bar{f}_\beta$

The above results are in agreement with the observations made by Gillespie (1962), that the lone pair of electrons interact more strongly with the neighbouring electron pairs than the bond pair of electrons. The fact that the greater repulsion of the lone pair decreases the equatorial bond angles more than the axial bond angle from their ideal values, is well reflected in the higher value of the equatorial bending force constant.

The mean amplitudes of vibration calculated here are in very good agreement with the values reported by one of the authors (Krishna Pillai *et al* 1965) and with the observed values from electron diffraction data (Kimura and Bauer 1963). The higher value for the equatorial-equatorial non bond mean amplitude of vibration compared to the equatorial-axial non bond mean amplitude of vibration is consistent with the higher equatorial being frequency (557 cm^{-1}). Further the value of σ_η is also higher than that of σ_β. It may therefore be concluded that the presence of lone pair of electron in the equatorial site (as 3*d* electrons) gives rise to a higher equatorial bending force constant, a higher equatorial-equatorial non bond mean amplitude of vibration and higher equatorial bending mean amplitude All these results indicate the possibility of an incomplete intramolecular inversion in SF_4 molecule (Chantry and Ewing 1962).

In conclusion, it may be said that the modified kinematic procedure although approximate, may nevertheless be used to obtain a reasonable good set of potential field of a molecule.

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